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Low-Temperature Mobility of the Electron Bubble in Dilute He^3-He^4 Mixtures and Pure He^3 †

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Recent low-temperature measurements of the mobility of negative ions in dilute He^3-He^4 mixtures are explained. A new method based on the Boltzmann equation is used to derive the general formula for the drag force of a heavy impurity in an arbitrary gas. It is shown that the structure of the negative ion (electron bubble) depends on the He^3 concentration C_3 and temperature. Also, for C_3 above about 1% the distortion of the He^3 distribution by the moving ion becomes important. The application of our theory to pure, highly degenerate He^3 shows that the mobility remains finite at $T=0$ and rises with temperature. Both results agree with experiment.

I. INTRODUCTION

Recently, Meyer and Neeper[1,3] have studied the mobility of positive and negative ions in dilute He^3-He^4 mixtures with atomic He^3 concentration C_3 ranging 1.5×10^{-4} to $4.4.\times10^{-2}$. In their temperature region $(0.05\,^\circ\mathrm{K} \le T \le 0.5\,^\circ\mathrm{K})$ the mobility is determined by He^3 scattering except in the very dilute case, where a small correction for phonon scattering is necessary. Some of the experimental results for $\mu_0 C_3$, where μ_0 is the low-field mobility,[3] are shown in Fig. 1. One sees that the product $\mu_0 C_3$ does not depend very much on concentration. The remaining variation of $\mu_0 C_3$ with concentration, its rather complicated temperature dependence, and the vast difference in the behavior of the positive and negative ions impose severe restrictions on a theoretical explanation. We present a theory that explains some of the observed features and yields quite good agreement with the experimental results on negative ions.

For our purposes we assume that the He^3-He^4

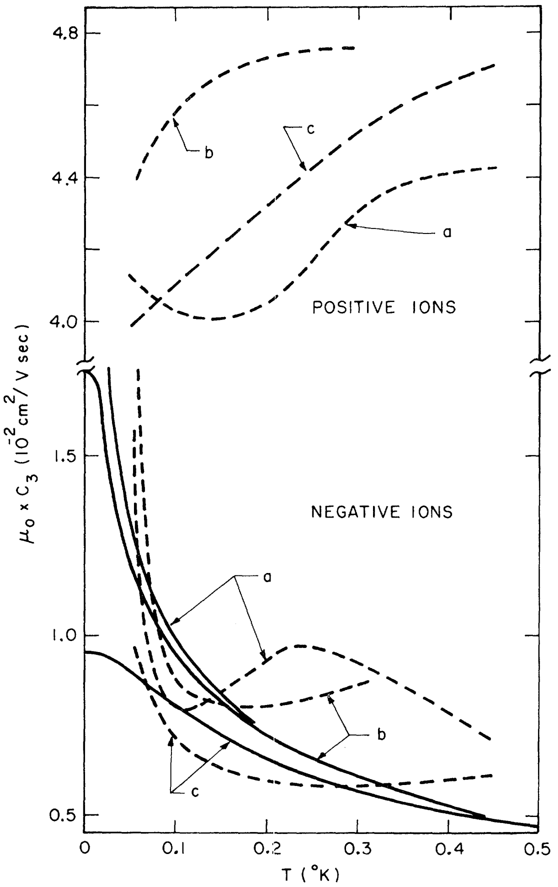

FIG. 1. The product of atomic He^3 concentration C_3 and low-field mobility μ_0, as a function of temperature. The solid curves are calculated with the simple theory using an ion radius of 28 Å, while the dashed curves are measurements from Refs. 1 and 2 (corrected for phonons). (a) $C_3=1.8\times10^{-4}$; (b) $C_3=2.9\times10^{-3}$; (c) $C_3=2.9\times10^{-2}$.

mixture can be described as a Fermi gas, the superfluid He^4 acting merely as an inert background that dilutes the He^3 quasiparticles. This picture, proposed by Landau and Pomeranchuk,[4] has proved successful in many cases. Interactions between the He^3 quasiparticles are taken into account only through a slightly temperature-dependent effective mass m^*. Effects that become important for large ion density are neglected; such a drag effect has been discussed recently by Bailyn and Lobo.[5]

In Sec. II we derive a general expression for the drag force which acts on a heavy impurity moving through a dilute gas of arbitrary particles or quasiparticles. This is done by using the Boltzmann collision integral to calculate the average rate of momentum transferred to the gas. To lowest-order in the drift velocity, the method leads to the same formula as that derived by Davis and Dagonnier[6] with a Fokker-Planck equation. Our treatment is simpler and indicates that the formula applies in a wider range. The connection to a different approach used by a number of authors[7-11] is shown. Only the recent treatment by Baym, Barrera, and Pethick[11] leads to a general and correct result.

In Sec. III the mobility for impurities with radius a small compared to the mean free path λ of the He^3-He^4 mixture ("Knudsen limit") is evaluated numerically. We take a simple hard-sphere scattering potential for the impurity. The procedure yields only very qualitative agreement with the measurements on negative ions ("electron bubbles") and no agreement with positive ions.

We propose two effects which together can account for most of the features observed with negative ions. It is shown that, at low temperature, He^3 atoms get adsorbed at the surface of the negative-ion complex, thus altering its scattering cross section. Similar ideas were put forward by Rayfield[12] and Dahm[13] to explain the reduction of the critical velocity for vortex-ring creation by negative ions when He^3 is added to superfluid He^4. A simple model for the modified electron bubble leads to an expression for the bubble radius and the average number of adsorbed He^3 atoms as a function of the chemical potential of the He^3 solution. A suitable choice of two parameters allows us to reproduce the temperature dependence of the low-field mobility quite well for temperatures above about 0.1 °K. If one adjusts the radius of the ion structure to the low-concentration data, the mobility at the higher concentrations comes out to be altogether too low.

This discrepancy can be removed in part by including deviations from the Knudsen limit. In the Knudsen limit the distortion of the distribution of gas particles by the moving ion is neglected. In Sec. IV this distortion is computed to first order in a/λ and in the drift velocity V of the ion for a Boltzmann gas of real particles. At a He^3 concentration $C_3=2.9\%$, the correction to the mobility is about 33%.

In Sec. V the results are applied to pure and highly-degenerate He^3. Our treatment shows that the mobility remains finite at zero temperature in agreement with experiments by Anderson *et al.*,[14] which extend down to 0.03 °K. Since three authors[15-17] have predicted a T^{-2} dependence of the mobility at low temperature, we examine the approximations involved for this case more closely. The Knudsen correction leads to a contribution proportional to T^2 reducing the drag force. An estimate of the magnitude of the correction based upon the calculations in Sec. IV gives qualitative agreement with experiment.

Finally, in Sec. VI the deficiencies of our treatment are discussed, and some brief remarks on positive ions are made.

II. MOBILITY OF A HEAVY IMPURITY IN A DILUTE GAS

The analysis in this section will be presented in such a way that it applies to the mobility of a heavy impurity in a dilute system of an arbitrary kind of elementary particles or quasiparticles. For simplicity the term "quasiparticle" will always be used for the scatterers.

Assume that the distribution functions n and f for the quasiparticles and the impurity, respectively, can be determined by a system of two coupled Boltzmann equations. The mobility μ_0 in an isotropic medium is defined by the relation $\vec{V}=\mu_0\vec{F}$, where $\vec{F}$ is the external force acting on the impurity, and $\vec{V}=\langle\vec{v}\rangle$ is the thermal average velocity of the impurity. In the stationary state $\vec{F}$ is equal to the average rate of momentum transferred by the impurity to the gas, given by

$$\frac{\partial \vec{P}}{\partial t}=\vec{F}=g\sum_{\vec{p}}\vec{p}\left(\frac{\partial n}{\partial t}\right)_{\text{coll}} . \qquad (1)$$

Here g is the spin degeneracy factor of the quasiparticles and n is to be taken in the vicinity of the impurity. If we assume that the impurity obeys Boltzmann statistics, the collision integral has the form

$$\left(\frac{\partial n}{\partial t}\right)_{\text{coll}}=\int d^3v\,d^3v'\sum_{\vec{p}'}[f'n'(1\pm n)-fn(1\pm n')] \times\Gamma(\vec{p}\,\vec{v}\to\vec{p}'\vec{v}') . \qquad (2)$$

The impurity is characterized by its velocity $\vec{v}$, while the quasiparticles are characterized by their momenta $\vec{p}$. It is assumed that the probability $\Gamma(\vec{p}\,\vec{v}\to\vec{p}'\vec{v}')$ for a transition from the initial state $\vec{p},\vec{v}$ to the final state $\vec{p}',\vec{v}'$ is equal to $\Gamma(\vec{p}'\vec{v}'\to\vec{p}\,\vec{v})$ (detailed balance). We have introduced the notation $f'=f(\vec{v}')$ and $n'=n(\vec{p}')$. Equation (2) can be simplified considerably if one may neglect the recoil of the impurity in computing the momentum transfer $\vec{p}-\vec{p}'$ at a single collision. This amounts to setting

$$\vec{v}'=\vec{v} , \qquad (3)$$

$$f=\delta^{(3)}(\vec{v}-\vec{V}) , \qquad (4)$$

in Eqs. (1) and (2), and yields

$$\vec{F}=g\sum_{\vec{p}\vec{p}'}\vec{p}(n'-n)\,\Gamma(\vec{V};\vec{p}\to\vec{p}') . \qquad (5)$$

We have introduced

$$\Gamma(\vec{p}\,\vec{v}\to\vec{p}'\vec{v}')=\delta^{(3)}(\vec{v}-\vec{v}')\,\Gamma(\vec{v};\,\vec{p}\to\vec{p}') . \qquad (6)$$

If the quasiparticles have an energy spectrum of the form $\epsilon=p^2/2m^*$, the condition

$$M\gg m^* , \qquad (7)$$

where M is the effective mass of the impurity, ensures that the approximations (3) and (4) can be used.

Equation (5) has several interesting features: (i) It is valid in the zero-temperature limit of a Fermi gas. The implications of this fact for pure He^3 are discussed in Sec. V, where also a more careful examination of the approximations (3) and (4) for this case is presented. (ii) Equation (5) is valid for arbitrary velocities $\vec{V}$. (iii) By interchanging the summations over $\vec{p}$ and $\vec{p}'$ in one of the terms in Eq. (5) one obtains

$$\vec{F}=g\sum_{\vec{p}\vec{p}'}n(\vec{p}'-\vec{p})\,\Gamma(\vec{v};\,\vec{p}\to\vec{p}') . \qquad (8)$$

This equation can be interpreted in a very intuitive way as the average momentum transfer at a single collision summed over all scattering events. Equation (8) has been used previously by Arkhipov,[7] Fetter,[8] Wang,[9] Schwarz and Stark,[10] and Baym *et al.*[11]

The transition rate Γ may have an intrinsic $\vec{V}$ dependence, pointed out already by Baym *et al.*[11] In the rest frame of the impurity the kinematic constraint for elastic collisions is given by $\tilde{\epsilon}'=\tilde{\epsilon}$. (In this section all quantities in the impurity rest frame are marked by tildes.) If Galilean relativity holds for the quasiparticles (a necessary condition for this is $\epsilon=p^2/2m^*$), one can write $\tilde{\epsilon}=\epsilon(\tilde{p})$ and is led to $\tilde{p}'=\tilde{p}$. Thus the usual elastic kinematics holds and Γ has no $\vec{V}$ dependence. If the gas is not Galilean-invariant, as is the case for collective excitations, $\tilde{p}'$ is not equal to $\tilde{p}$ in general. In this case, great care has to be taken in treating the kinematics built into Γ. At this point the authors of Refs. 9 and 10 introduced errors. The treatment of the authors of Refs. 7 and 8, although leading to the correct result, is valid only for an impurity in a superfluid moving with the superfluid part.

To cope with the above mentioned difficulty, Eq. (5) is better suited than Eq. (8), since the term $(n'-n)$ is explicitly of order $\vec{V}$, so that one can neglect the intrinsic $\vec{V}$ dependence of Γ at low velocities. The kinematic constraint for elastic scattering is given in the rest frame of the quasiparticle gas by

$$\epsilon' - \vec{p}' \cdot \vec{V} = \epsilon - \vec{p} \cdot \vec{V} \quad . \tag{9}$$

Thus,we obtain from Eq. (5) to first-order in $\vec{V}$

$$\vec{F} = g \sum_{\vec{p}\,\vec{p}'} \vec{p} \, \{ n[\hat{p}', \, \epsilon + \vec{V} \cdot (\vec{p}' - \vec{p})] - n(\hat{p}, \epsilon) \} \, \Gamma(0; \vec{p} \rightarrow \vec{p}') . \tag{10}$$

Here n is explicitly allowed to be anisotropic. It is assumed, however, that when $\vec{V}$ is zero, n is given by the isotropic equilibrium distribution function n_0. Therefore, the anisotropy of n is only a consequence of the distortion of n_0 by the moving impurity and is of order $\vec{V}$. Also we assume that to first order in $\vec{V}$ one can write

$$n(\hat{p}', \epsilon) - n(\hat{p}, \epsilon) = \vec{V} \cdot (\vec{p}' - \vec{p}) \, \delta n(p) \quad . \tag{11}$$

The quantity δn defined in Eq. (11) can be neglected in the Knudsen limit and will be computed for a spherical impurity in Sec. IV. Now, replace sums by integrals in Eq. (10), and express Γ in terms of the incoming quasiparticle current $v_{\mathrm{rel}}/\mathrm{vol.}$, the density of final states ρ_f, and the differential scattering cross section $d\sigma/d\Omega$:

$$\begin{aligned} \Gamma(0; \vec{p} \rightarrow \vec{p}') &= \frac{v_{\mathrm{rel}}}{\mathrm{vol}\, \rho_f} \, \delta(\epsilon - \epsilon') \, \frac{d\sigma}{d\Omega_\theta}(p, \theta) \\ &= \left| \frac{d\epsilon}{dp} \right| \frac{(2\pi\hbar)^3}{(\mathrm{vol})^2 p^2} \, \delta(p - p') \, \frac{d\sigma}{d\Omega_\theta}(p, \theta) \quad . \end{aligned} \tag{12}$$

Expanding the curly bracket in Eq. (10) to first order in $\vec{V}$ and inserting (11) and (12) lead to

$$\begin{aligned} \vec{F} = g \int \frac{d^3p}{h^3} \; & d\Omega_\theta (\hat{V} \cdot \vec{p}) [V \cdot (\vec{p}' - \vec{p})] \\ & \times \left(\frac{dn_0}{d\epsilon} + \delta n \right) \left| \frac{d\epsilon}{dp} \right| \frac{d\sigma}{d\Omega_\theta} \quad . \end{aligned} \tag{13}$$

The fact that $\vec{F}$ is parallel to $\vec{V}$ was used. Equation tion (13) is valid as long as

$$V \ll \bar{v} \tag{14}$$

holds, where $\bar{v}$ is the average velocity of those quasiparticles taking part in the scattering. Performing the angular integrations in Eq. (13) finally leads to

$$\frac{F}{V} = \mu_0{}^{-1} = - \frac{g}{6\pi^2\hbar^3} \int dp \, p^4 \left(\frac{dn_0}{d\epsilon} + \delta n \right) \left| \frac{d\epsilon}{dp} \right| \sigma_{Tr}(p) \quad , \tag{15}$$

where $$\sigma_{Tr} = \int d\Omega_\theta \frac{d\sigma}{d\Omega_\theta} (1 - \cos\theta) \tag{16}$$

is the "momentum-transfer" cross section. In the Knudsen limit, Eq. (15) reduces to

$$\frac{F}{V} = \mu_0^{-1} = \frac{g}{6\pi^2\hbar^3} \int dp \, p^4 \left| \frac{dn_0}{dp} \right| \sigma_{Tr}(p) \quad . \tag{17}$$

Equation (17) has been derived by Davis and Dagonnier[6] by a different method based on the Boltzmann equation. Their treatment is valid only for drift velocities $\vec{V}$, which are of the order of the thermal velocity $(kT/M)^{1/2}$ [instead of (14)], and for the case where the motion of the impurity can be described by a Fokker-Planck equation. We believe that the approximations (3) and (4) in this context are not always equivalent to a Fokker-Planck description. Any choice of f with a thermal spread small compared to $\bar{v}$ leads to the same result (see Sec. V). In Eq. (8) one cannot in general replace $\Gamma(\vec{V}; \vec{p} \rightarrow \vec{p}')$ immediately by its value at $V = 0$.[11]

It is easy to see that in the Boltzmann region and Knudsen limit [conditions (3) and (4) are now not needed] the drag force F is proportional to the density N of quasiparticles. One can prove this for arbitrary kinds of scattering (elastic or inelastic). Omitting in Eq. (2) the quantum-statistical factors $1 \pm n$ and $1 \pm n'$ and inserting the Boltzmann distribution

$$n_0 = \tfrac{1}{2} N (2\pi\hbar^2\beta/m^*)^{3/2} e^{-\beta p^2/2m^*} \quad , \tag{18}$$

($\beta \equiv 1/kT$), one immediately sees that $(\partial n/\partial t)_{\mathrm{coll}}$ is proportional to N. As a consequence, F is proportional to N, and the quantity $\mu_0 N$ does not depend on N.

III. STRUCTURE OF THE ELECTRON BUBBLE IN DILUTE He^3-He^4

The negative ion in helium consists of an electron inside a bubble of about 20 Å radius. This structure is energetically favorable because of the large zero-point energy of the electron. We have evaluated Eq. (17) numerically, treating the bubble as a hard sphere with respect to He^3 scattering. The results obtained for a scattering radius[18] $a = 28$ Å are plotted in Fig. 1 (solid curves) for three concentrations. We have summed 22 partial waves. The value of $a\bar{k}$, where $\bar{k}$ is the average scattering wave number, lies between about two and ten in this calculation. Thus by taking the short-wavelength limit for the cross section, one would introduce a notable error.

The experimental results from Refs. 1 and 2 have been included in Fig. 1. Although this theory reproduces some of the general features, agreement is certainly not too good. The data for $C_3 = 1.8\times10^{-4}$ and $C_3 = 2.9\times10^{-3}$, above about 0.1 °K, lie to a good approximation in the Boltzmann region and Knudsen limit (see also Sec. IV). Since $\mu_0 C_3$ is not really independent of concentration in the experiments, one cannot hope to resolve the discrepancies solely by choosing a better scattering cross section. (See the conclusions in Sec. II.) Inelastic contributions, in particular, cannot account for the unusual temperature dependence of $\mu_0 C_3$.

In the light of this result, we are forced to conclude that the structure of the negative-ion complex changes with He^3 concentration and/or temperature.[19] The zero-point energy of a He^3 atom in a He^3-He^4 mixture exceeds that of a He^4 atom by about 4.3 °K. Dahm[13] therefore proposed that He^3 atoms tend to condense on the surface of an electron bubble, where they are able to reduce their zero-point energy. We wish to offer a simple description of this adsorption similar to Andreev's[20] theory of the surface tension of dilute He^3-He^4 mixtures.

At zero pressure, the contribution of the electron bubble to the thermodynamic potential in the crudest approximation is given by

$$\Omega_s = \hbar^2 k_0^2/2m_e + 4\pi\gamma R^2 \quad . \tag{19}$$

Here m_e is the electron mass, k_0 the momentum eigenvalue of the electron, γ the surface tension of the mixture, and R the bubble radius. Assuming that the electron wave function penetrates only insignificantly into the surrounding fluid, we have $k_0 = \pi/R$ for the ground state. Minimizing Ω_s with respect to R then leads to

$$R^4 = \pi\hbar^2/8\gamma m_e ; \qquad \Omega_s = 8\pi R^2\gamma \quad . \tag{20}$$

At low temperature, the surface tensions of pure He^3 and He^4 are given approximately by $\gamma_3 = 0.15$ erg/cm^2 and $\gamma_4 = 0.35$ erg/cm^2. As a consequence, the radius of the electron bubble in He^3 is slightly larger and its free energy is considerably lower than in He^4. Therefore, it is energetically favorable for He^3 atoms in a He^3-He^4 mixture to condense on the bubble surface. Treating Ω_s as a surface contribution to the thermodynamic potential, one obtains for the excess number of He^3 atoms at the bubble surface,

$$N_s = -\left(\frac{\partial\Omega_s}{\partial\mu}\right)_T = -4\pi R^2\left(\frac{\partial\gamma}{\partial\mu}\right)_T \quad . \tag{21}$$

Here μ is the chemical potential of the He^3 atoms, which is the same in the bulk and at the surface. Equation (21) is similar to the Gibbs equation, which is well known in surface physics and chemistry.[21]

To obtain $(\partial\gamma/\partial\mu)_T$ a model for the surface is needed. We treat the He^3 atoms at the surface as a two-dimensional Fermi gas with energy spectrum

$$\epsilon = -\epsilon_s + p^2/2m_s \quad , \tag{22}$$

where m_s is an appropriate effective mass to be chosen below. The energy is measured with respect to the ground state of He^3 in the bulk, so that ϵ_s represents a surface binding energy. In the highly degenerate limit, the chemical potential and the thermodynamic potential for the surface gas are easily calculated. One obtains

$$\mu = -\epsilon_s + \pi\hbar^2 N_s/(4\pi R^2 m_s) \quad , \tag{23}$$

$$E_s - \mu N_s = -\pi\hbar^2 N_s^2/(8\pi R^2 m_s) \quad . \tag{24}$$

Equations (23) and (24) are valid for $(kT)^2 \ll (\mu + \epsilon_s)^2$. We now make the assumption that $E_s - \mu N_s$ is identical with Ω_s up to a constant which is determined by requiring $\gamma = \gamma_4$ for $N_s = 0$. Equations (20), (21), and (24) then give

$$\frac{N_s}{4\pi R^2} = -\frac{d\gamma}{d\mu} = \left(\frac{4m_s}{\pi\hbar^2}\left[(\gamma\gamma_4)^{1/2} - \gamma\right]\right)^{1/2} \quad . \tag{25}$$

Integrating Eq. (25) leads to

$$\sqrt{\gamma_4}\,\sin^{-1}\left[2(\gamma/\gamma_4)^{1/2} - 1\right] - \left[(\gamma\gamma_4)^{1/2} - \gamma\right]^{1/2} + B = -\left(\frac{4m_s}{\pi\hbar^2}\right)^{1/2}\mu \quad , \tag{26}$$

where B is a constant. Equations (25) and (26) give γ and N_s as functions of the chemical potential μ which can be obtained from the temperature and concentration C_3.[22] To determine the parameters B and m_s we proceeded in the following manner: At $C_3 = 1.8\times10^{-4}$ the two values for $\mu_0 C_3$ measured above $T = 0.27$ °K (see Fig. 2) can be described with our theory if a is taken to be 21.6 Å. Thus, the radius for the ion complex remains essentially constant above this temperature. Therefore, we assume that in our model the surface states become emptied at $T = 0.27$ °K, which corresponds at this concentration to $\mu \approx -1.5$ °K. Another condition is obtained by assuming that $\gamma = \gamma_3$ holds at the point where pure He^3 starts to separate out at $T = 0$ ($C_3 = 6\%$, $\mu \approx 0.37$ °K). Imposing these conditions on Eq. (26) we find $B = -0.105$ erg$^{1/2}$ and $m_s = 14.8\times10^{-24}$ g, which is practically equal to the effective mass of pure He^3.

We still need the scattering radius a of the ion structure. The simplest assumption is

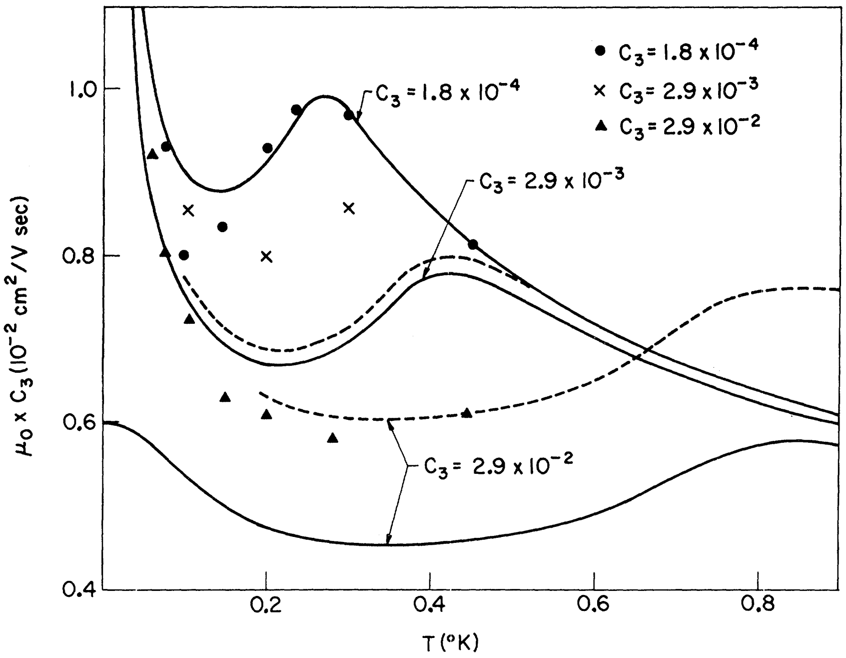

FIG. 2. The product $\mu_0 C_3$ as a function of temperature for negative ions. The solid curves are evaluated taking into account the change of scattering radius, while the dashed curves show in addition the correction to the Knudsen limit. The experimental points have been taken from Refs. 1 and 2.

$$a = R + r_0 + v_s / 4\pi R^2 N_s \ , \qquad (27)$$

where r_0 is the scattering radius of a He^3 atom (≈ 2.3 Å) and v_s is the volume of a He^3 atom at the surface. We expect v_s to be somewhat larger than the atomic volume of a He^3 in the bulk ($\approx 60\ Å^3$). In order to obtain a reasonable fit with the experiments we took $v_s = 83\ Å^3$. Figure 3 shows the scattering radius a as a function of μ. The numerical results for $\mu_0 C_3$, obtained in the same way as before, are plotted in Fig. 2 (solid curves) together with the corresponding measurements. The sudden change in slope in the curve of Fig. 3 arises as a consequence of treating the surface system as completely degenerate, and is correct only in the zero-temperature limit (which for negative μ also corresponds to $C_3 \to 0$). At finite temperature and concentration there will be some rounding. We have roughly included this effect in Fig. 2 by rounding off the peaks of the curves. Since with increasing temperature the chemical potential decreases more rapidly at low concentrations than at high ones, the peaks move from lower to higher temperature as the concentration increases. This seems to be consistent with experiment. The somewhat too low theoretical mobilities at the higher concentrations will be discussed in Sec. IV.

We might propose the following explanation for the rather striking discrepancies below 0.1 °K. It is well known that a dilute mixture can take a rather long time to attain its equilibrium surface tension at a freshly formed surface.[23] Measurements on other binary systems indicate that the surface tension initially has the value of the pure solvent, and that the relaxation time may lie between a fraction of a millisecond and several days. It is possible that, for the mixture considered here, the relaxation time below about 0.1°K becomes of the order of the travel time of the ion. Owing to the increase in surface tension, μ_0 could then become as large as twice the value predicted by our equilibrium theory. The mobility should, however, remain finite in the zero-temperature limit.

Although our model leads to some plausible conclusions, we warn the reader not to take the details at this time too seriously. Equations (19)–(23) alone lead to almost the same results if one

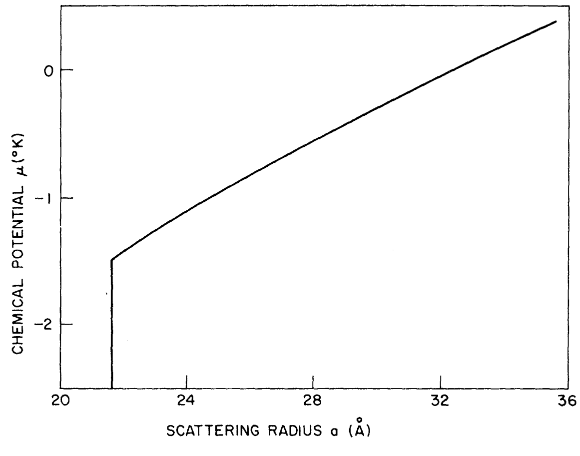

FIG. 3. Ion scattering radius a as a function of chemical potential μ.

assumes that ϵ_s is a constant equal to $-1.5\,^\circ$K. Then one has to take $m_s \approx 20\times 10^{-24}$g and $v_s \approx 70\,\text{Å}^3$. It is also to be anticipated that m_s and v_s depend to some extent on N_s. We hope to be able to generalize the model to finite pressure and also to use it for the calculation of the surface tension of dilute mixtures at a free surface.

IV. CORRECTION TO THE KNUDSEN LIMIT

When the impurity moves through the gas, strictly speaking, it does not see the equilibrium distribution of particles. The particles scattered off the impurity will undergo collisions and thus change the distribution in the vicinity of the impurity. For instance, those particles scattered into the forward direction with respect to the moving impurity have a somewhat higher average momentum than the rest of the gas. By collision they will transfer some forward momentum to other particles and so "clear the path" for the impurity to some extent. The corresponding process takes place in the backward direction, but since the backscattered particles have a smaller average momentum, it is less efficient. The net effect is of order V and reduces the drag force.

The effect becomes negligible as the mean free path λ of the gas particles becomes very large compared to the dimension a of the impurity. As λ becomes smaller, the effect leads to a situation where more and more gas particles in a layer of thickness λ move along with the impurity. Finally when $\lambda \ll a$ holds, the hydrodynamic limit is reached. Calculations in both limits are relatively simple, but get extremely complicated in the intermediate region.[24] Such computations have been performed predominantly for hypersonic speeds,[25] where they are of interest to astrophysicists and space scientists. Some literature on low-velocity calculations may be found in a review article by Grad.[26]

We are interested in calculating a first correction to the distribution of gas particles around a slowly moving spherical impurity of radius a when a/λ is finite but small compared to 1. To do this, we introduce an approximation method for solving the Boltzmann equation similar to the one proposed by Jaffé[27] and apply it to a spin-$\frac{1}{2}$ Boltzmann gas. The Boltzmann equation can be written

$$\frac{\partial n}{\partial t} + \frac{\vec{\mathrm{p}}}{m^*}\cdot\frac{\partial n}{\partial \vec{\mathrm{r}}} + \vec{F}_0\cdot\frac{\partial n}{\partial \vec{\mathrm{p}}} \equiv \frac{\partial n}{\partial s} = I_1(n) + I_2(n,n), \qquad (28)$$

where the collision integrals for He^3 impurity and He^3-He^3 scattering, respectively, are given by

$$I_1(n) = \int d\Omega_\theta (n' - n)\frac{p}{m^*}\frac{d\sigma}{d\Omega_\theta}(p,\theta) \;; \qquad (29)$$

$$I_2(n_a, n_b) = 2h^{-3}\int d^3p_1 \int d\Omega' \left|\frac{\vec{\mathrm{p}} - \vec{\mathrm{p}}_1}{m^*}\right| \frac{d\sigma_0}{d\Omega'} \times [n_a(\vec{\mathrm{p}}')n_b(\vec{\mathrm{p}}_1') - n_a(\vec{\mathrm{p}})n_b(\vec{\mathrm{p}}_1)] \;. \qquad (30)$$

Here $d\sigma_0/d\Omega$ is the differential cross section for a binary collision with initial momenta $\vec{\mathrm{p}}, \vec{\mathrm{p}}_1$ and final momenta $\vec{\mathrm{p}}', \vec{\mathrm{p}}_1'$. In estimating the relative order of magnitude of I_1 and I_2 we note that the net effect of the impurity is to replace the total cross section of all the gas particles that fit into its volume by its own cross section. Since in the equilibrium state I_2 is zero, we have

$$I_2/I_1 \sim a^3 N\sigma_0/\sigma \sim a/\lambda \;, \qquad (31)$$

where N is the density of gas particles, σ_0 and σ are total cross sections, and $\lambda = (N\sigma_0)^{-1}$ is the mean free path. Assume that n can be expanded in a convergent series $n = n_0 + n_1 + n_2 + \cdots$, where n_0 is the equilibrium distribution and n_i is of order $(a/\lambda)^{i-1}$ for $i \geq 1$. Using the symbolic derivative $\partial/\partial s$ defined in Eq. (28), we obtain

$$\frac{\partial n_0}{\partial s} = 0 \;;$$
$$\frac{\partial n_1}{\partial s} = I_1(n_0) \;; \qquad (32)$$
$$\frac{\partial n_2}{\partial s} = I_1(n_1,) + I_2(n_1, n_0) + I_2(n_0, n_1) \;;$$
$$\cdots\cdot$$

The first two equations correspond to the Knudsen limit.

It is now convenient to work in the rest frame of the impurity with the origin at the center of the impurity. The force field $\vec{\mathrm{F}}_0$ is zero in our case, and in the stationary state n does not depend on time. Therefore the left-hand sides of Eqs. (32) can be written as $m^{*-1}\vec{\nabla}\cdot(\vec{\mathrm{p}}n_i)$. Transforming Eqs. (32) into integral form leads to

$$n_1 = \frac{m^*}{p}\frac{I_1(n_0)}{r^2}\,\delta^{(2)}(\hat{p},\hat{r}) \;, \qquad (33)$$

$$n_2 = \frac{m^*}{p}\frac{I_1(n_1)}{r^2}\,\delta^{(2)}(\hat{p},\hat{r}) + \frac{m^*}{4\pi p}\int d^3r' \times \frac{[I_2(n_1(\vec{\mathrm{r}}'), n_0) + I_2(n_0, n_1(\vec{\mathrm{r}}'))]\,\hat{p}\cdot(\vec{\mathrm{r}} - \vec{\mathrm{r}}')}{|\vec{\mathrm{r}} - \vec{\mathrm{r}}'|^3} \;. \qquad (34)$$

The two-dimensional δ function restricts all the particles that have been scattered off the impurity to radial paths away from the origin. At this point we neglect the finite size of the impurity, which is consistent to first order in a/λ.

To obtain n_1 from Eq. (33), one has to evaluate $I_1(n_0)$ in much the same way as the similar collision integral in Sec. II was computed. One easily finds to first order in V

$$I_1(n_0) = (\vec{\mathrm{p}}\cdot\vec{\mathrm{V}})\left|\frac{dn_0}{dp}\right|\sigma_{Tr} \ . \tag{35}$$

Inserting for n_0 the Boltzmann distribution (18), and using Eqs. (33) and (35) then lead to

$$n_1 = (\vec{\mathrm{p}}\cdot\vec{\mathrm{V}}/r^2)\,\beta n_0\sigma_{Tr}\,\delta^{(2)}(\hat{p},\hat{r}) \ . \tag{36}$$

Equation (34) can be further simplified. It turns out that after averaging suitably over angles one can introduce two quantities j_1 and j_2 depending only on p, so that one can write approximately

$$I_2(n_1, n_0) + I_2(n_0, n_1)$$

$$= (\hat{r}\circ\vec{\mathrm{V}}/r^2)[j_1(p) + j_2(p)\delta^{(2)}(\hat{p},\hat{\mathrm{r}})] \ . \tag{37}$$

With the help of Eq. (37) the spatial integral in Eq. (34) can be evaluated. Note that I_2 is zero inside the impurity, so that the integration is restricted to the exterior of a sphere with radius a around the origin (here the finite size of the impurity comes into play). Also $I_1(n_1)$ is zero. We obtain for n_2 on the surface of the impurity

$$n_2(\vec{\mathrm{p}}) = -\frac{m^*}{p}\frac{\vec{\mathrm{p}}\cdot\vec{V}}{a}\left(\tfrac{1}{3}j_1(p) + \frac{1}{4\pi}j_2(p)\right) \ . \tag{38}$$

Now calculate δn as defined in Eq. (11), with $n = n_0 + n_1 + n_2$. Clearly n_0 and n_1 do not contribute. Equations (38) and (11) give

$$\delta n = -\frac{m^*}{p^3 a}\left(\tfrac{1}{3}j_1(p) + \frac{1}{4\pi}j_2(p)\right) \ . \tag{39}$$

To evaluate j_1 and j_2 from Eq. (37) one has to calculate I_2. Inserting Eq. (36) into Eq. (30) and assuming isotropic interparticle scattering, one finds to first order in V,

$$I_2(n_1, n_0) + I_2(n_0, n_1) = \tfrac{1}{4}N^2\left(\frac{2\pi\hbar^2\beta}{m^*}\right)^3\beta\sigma_0\sigma_{Tr}\,\frac{\hat{r}\cdot\vec{\mathrm{V}}}{2\pi r^2}\int\frac{d^3p_1}{h^3}\exp\left(-\beta\frac{p^2+p_1^2}{2m^*}\right)$$

$$\times\ d\Omega'\left|\frac{\vec{\mathrm{p}}-\vec{\mathrm{p}}_1}{m^*}\right|\ p_1'\delta^{(2)}(\hat{p}_1',\hat{r}) + p'\delta^{(2)}(\hat{p}',\hat{r}) - p_1\delta^{(2)}(\hat{p}_1,\hat{r}) - p\delta^{(2)}(\hat{p},\hat{r}) \ . \tag{40}$$

The last term in brackets contributes to j_2 while the rest contributes to j_1. In evaluating the integral in Eq. (40) we have from the beginning averaged over all angles. We obtain after a somewhat tedious but straightforward calculation:

$$j_1(p) \approx -\tfrac{1}{2}N\left(\frac{2\pi\hbar^2\beta}{m^*}\right)^{3/2}\sigma_0\sigma_{Tr}$$

$$\times\frac{n_0}{(2\pi\hbar)^3}\left[\tfrac{3}{4}\sqrt{\pi}\left(\frac{2m^*}{\beta}\right)^{3/2} - 1.83p\,\frac{2m^*}{\beta}\right];$$

$$\tag{41}$$

$$j_2(p) \approx -\tfrac{1}{2}N\left(\frac{2\pi\hbar^2\beta}{m^*}\right)^{3/2}\sigma_0\sigma_{Tr}\,\frac{n_0}{2\pi^2\hbar^3}\left[2p\,\frac{2m^*}{\beta} + \tfrac{2}{3}p^3\right]$$

Now insert Eq. (39) together with Eqs. (41) into the mobility formula (15). Taking σ_{Tr} in the short-wavelength limit where it is equal to πa^2 we are led to

$$F = \tfrac{2}{3}a^2VN\left(\frac{2\pi m^*}{\beta}\right)^{1/2}(1 - 0.36a\sigma_0N)$$

$$= F_0(1 - 0.36a/\lambda) . \tag{42}$$

A realistic estimate for the He^3-He^3 scattering radius is about 2.3 Å.[28] At $T = 0.3$ °K, the average wave number of the He^3 quasiparticles at low concentration is 0.3 $\mathrm{Å}^{-1}$. Then the total hard-sphere cross section is about $\sigma_0 \approx 5\times10^{-15}$ cm^2. Expressing the density N in terms of the atomic He^3 concentration C_3, we finally arrive at

$$F = F_0(1 - 0.39C_3a/\mathrm{Å}) \ . \tag{43}$$

Choosing $a = 22$ Å and $C_3 = 2.9\%$, the correction to the mobility turns out to be about 33%. Owing to the influence of higher-order corrections and the error introduced through the various approximations, we estimate the uncertainty of the correction term to be about 40% in this case. At $C_3 = 2.9\times10^{-3}$ the correction does not remove the discrepancy between theory and experiment, and at $C_3 = 1.8\times10^{-4}$ it is negligible.

Neeper and Meyer[2] have also obtained some mobility data for $C_3 = 4.4\%$. The results indicate that for $T > 0.1$ °K the values of μ_0C_3 are higher than for $C_3 = 2.9\%$. Our theory provides a simple explanation for this fact.

V. LOW-TEMPERATURE MOBILITY IN PURE He^3

Here we will first examine more closely the approximations (3), (4), and (14), which lead to the mobility formula (17) for the controversial case of a Fermi gas with energy spectrum $\epsilon = p^2/2m^*$ at zero temperature (see Refs. 6, 15–17). For an interacting system the treatment should be interpreted in the spirit of Landau's Fermi liquid theory. We assume that Eq. (7) holds.

Inserting Eq. (2) into Eq. (1) and interchanging dummy indices leads to

$$\frac{d\vec{P}}{dt} = g\int d^3v\, d^3v' \sum_{\vec{p}\vec{p}'} (\vec{p}' - \vec{p}) f n (1-n') \Gamma(\vec{p}\vec{v} \to \vec{p}'\vec{v}'). \tag{44}$$

Here $\vec{v}'$ appears explicitly only in Γ and implicitly through the kinematics in $\vec{p}'$. It is easy to see that $\vec{p}' = \vec{p}_0' + 0(m^*\vec{p}_0'/M)$, where $\vec{p}'$ is the outgoing fermion momentum calculated with approximation (3). If we assume that Γ does not depend too strongly on $\vec{v}'$, it is thus clear that setting $\vec{v}' = \vec{v}$ in Eq. (44) leads to a relative error of at most m^*/M, which we neglect.

Now set $\tilde{\vec{p}} = \vec{p} - m^*\vec{v}$, so that the kinematic constraint is given simply by $\tilde{p}' = \tilde{p}$. Introducing the scattering cross section in the same way as in (12), one obtains from Eqs. (6) and (44),

$$\vec{F} = g\int d^3v f(v) \int \frac{d^3\tilde{p}}{h^3}\, d\Omega_\theta\, (\tilde{\vec{p}} + m^*\vec{v})(\tilde{n}' - \tilde{n}) \frac{p}{m^*} \frac{d\sigma}{d\Omega_\theta}\ . \tag{45}$$

The notation $\tilde{n} = n(\tilde{\vec{p}} + m^*\vec{v})$ was used. For simplicity assume that $d\sigma/d\Omega$ does not depend on $\vec{p}$ and $\vec{v}$. At $T = 0$, n is given by $\theta(\epsilon_F - \epsilon)$, and one can write to third-order in $\vec{v}$,

$$\begin{aligned}\tilde{n}' - \tilde{n} \cong &- (\tilde{\vec{p}}' - \tilde{\vec{p}}) \cdot \vec{v}\, \delta(\epsilon - \epsilon_F) \\ &+ \tfrac{1}{2}[(\tilde{\vec{p}}' \cdot \vec{v})^2 - (\tilde{\vec{p}} \cdot \vec{v})^2 + (\tilde{\vec{p}}' - \tilde{\vec{p}}) \cdot \vec{v} m^* v^2] \frac{d}{d\epsilon}\, \delta(\epsilon - \epsilon_F) \\ &- \tfrac{1}{6}[(\tilde{\vec{p}}' \cdot \vec{v})^3 - (\tilde{\vec{p}} \cdot \vec{v})^3] \frac{d^2}{d\epsilon^2}\, \delta(\epsilon - \epsilon_F)\ .\end{aligned} \tag{46}$$

Inserting (46) into (45) and performing the angular integrations leads to

$$\vec{F} \cong g(\sigma_{Tr} p_F^4/6\pi^2\hbar^3)(\langle\vec{v}\rangle + \tfrac{2}{5}(m^{*2}/p_F^2)\langle\vec{v}^{\,3}\rangle). \tag{47}$$

Here we have used

$$\langle \circ\circ\circ \rangle = \int d^3v f(\vec{v}) \circ\circ\circ\ .$$

Since $M \gg m^*$ holds, the thermal width of f is certainly small compared to the Fermi velocity $v_F = p_F/m^*$. Therefore, $\langle\vec{v}^3\rangle$ can be replaced by $\langle\vec{v}\rangle^3$ in Eq. (47). One sees that the linear-force law holds as long as $\langle\vec{v}\rangle \equiv \vec{V}$ is small compared to v_F, which verifies Eq. (14) for this case. The linear term in (47) can be obtained directly from Eq. (17). The fact that the mobility in a Fermi system at zero temperature is finite might appear surprising. The situation is, however, analogous to that encountered in the residual resistance of metals: A Fermi system can perfectly well absorb energy even at $T = 0$.

Having shown that the theory developed in Sec. II is valid for a Fermi system at arbitrary temperature, we note that the low-temperature mobility measured by Anderson *et al.*[14] for negative ions in pure He^3 can be described by Eq. (17) taking a hard-sphere scattering potential with radius $a = 18.8$ Å at low pressure. The initial increase of the measured mobility with temperature can be explained qualitatively quite well by a correction to the Knudsen limit. Just as in the Boltzmann case, the first correction is proportional to a/λ. Unfortunately we were not able to compute the magnitude of the correction term for a degenerate Fermi system. Therefore, we can only give a rough estimate by using the results for a Boltzmann gas.[29] The mean free path λ is now given by $v_F\tau_\eta$ where τ_η is the appropriate mean free time. In He^3 we have $v_F = 5.38\times 10^3$cm/sec and $\tau_\eta T^2 \approx 1.5\times 10^{-12}$sec $(°\mathrm{K})^2$.[30] Inserting the resulting mean free path into Eq. (42) leads to

$$F = F_0[1 - 0.45(a/\text{Å})(T/°\mathrm{K})^2]\ . \tag{48}$$

Since the radius of the electron bubble depends on pressure, one can also test the dependence of the correction term on a. Both the temperature and pressure dependence are in qualitative agreement with experiment.

Recently Gould and Ma[31,32] attempted to explain the initial rise of the negative-ion mobility with temperature by including the Friedel density oscillations around an impurity in an interacting Fermi system. They found a contribution to the drag force of about the right order of magnitude proportional to $F_0 a T^2 \log T$. It seems very unlikely to us that a quantum correction should be more important for a large impurity than for a small one. We believe that the result arises as a consequence of the expansion made in Eq. (15) of Ref. 31 valid for small $a(k - k_F)$ and of dropping the leading term proportional to $1/a^2$ later on.

VI. DISCUSSION

We feel that the experimental results of Neeper and Meyer[1,2] and of Anderson *et al.*[14] leave us with the following unresolved problems.

(i) The temperature dependence of the positive-ion mobility in dilute He^3-He^4 mixtures (see Fig. 1) and in pure[14] He^3 remains unexplained. We believe that at least in dilute He^3-He^4 mixtures, but possibly also in pure He^3, the ion complex undergoes a change in size or structure with temperature. The positive-ion complex is usually considered as consisting of a "snowball" of high-density helium with a solid core around the highly polarizing ion. It is interesting to note that in He^3-He^4 the cross section decreases with temperature, while in He^3 it seems to increase at first. This is in fact what one might expect from the different solidification curves of He^3 and He^4, although to a lesser degree. To some extent the concentration dependence of $\mu_0 C_3$ in He^3-He^4 can be understood by a correction to the Knudsen limit.

(ii) According to theory the electron bubble is larger in He^3 than in He^4. To fit the experiments, however, we had to take scattering radii of 18.8 and 21.6 Å for the "bare" bubble in He^3 and dilute He^3-He^4, respectively.

(iii) For both kinds of ions the measured mobility in He^3-He^4 mixtures at the intermediate concentration $C_3 = 2.9\times10^{-3}$ is 10–15% higher than expected from the low and high concentration.

On the other hand, we were able to explain most of the striking features of the negative-ion mobility in He^3 and He^3-He^4 at low temperature by (a) deriving the general mobility formula in a new way which indicates a broader range of applicability, (b) including structure changes of the electron bubble in He^3-He^4 mixtures, and (c) calculating a correction to the Knudsen limit.

It now seems desirable to extend the measurements in He^3-He^4 to temperatures and concentrations beyond the range covered by Neeper and Meyer. In addition it would be interesting to find out whether relaxation effects are responsible for the sharp rise of the negative-ion mobility at low temperature, as proposed in Sec. III. In order to test this, one would allow the ions to become "aged" before measuring their mobility.

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Modification of the Minimum-Entropy-Production Principle*

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The description of the steady state by means of a minimum principle is given. Previous attempts to use the entropy production were successful only if the deviations from equilibrium were small. We show how entropy production can be defined so that the principle will hold for arbitrary deviations. The choice is further corroborated by a physical picture: That part of the entropy production which is due to the heat flow to the bath should be divided, not by the temperature of the bath, but by a different temperature. This temperature is determined as a function of the occupation probabilities. Unfortunately, this temperature cannot be defined in an invariant way. The definition is microscopic and holds only for systems that can be described by a linearized master equation. A proof is given that the generalized temperature used in the new entropy-production definition is higher than the equilibrium temperature, but less than or equal to the steady-state temperature. This proof is limited to a two-level system, for which a steady-state temperature can be defined, interacting with a heat reservoir and external radiation, as discussed in the text.

INTRODUCTION

A number of attempts have been made to characterize steady-state processes by a minimum principle similar to the principles used in equilibrium statistical mechanics. The majority of the steady-state methods have this in common: They utilize some dissipative quantity as the quantity that has to be minimized. Others are based on the idea of optimization of certain probabilities similar to the fundamental ideas used in equilibrium theory. To the last class belongs the method that has been proposed by Onsager and Machlup[1] and utilized by Kikuchi.[2] We will not consider this type of theory, which, though undoubtedly more fundamental, is extremely difficult to apply to a given system.

Methods utilizing the optimization of a dissipative quantity have been proposed as far back as 1911 by Ehrenfest.[3] One type of theory starts with the Boltzmann transport equation.[4-7] A second type, based on the Onsager reciprocal relations,[8] is of macroscopic nature. Finally there are microscopic theories of minimum entropy production proposed by Klein and Meijer[9, 10] based on the